

Influence of Radiation on the Molecular Structure of Natural Solid Bitumens

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Knowledge of the structure of natural solid hydrocarbons subjected to radiation impact is of significant fundamental and practical interest. Coals are best studied in this respect. They frequently include minerals with radioactive elements (Th and U). Results of study show that organic matter is substantially less enriched in carbon at a distance exceeding the range of α -particle path than in the immediate proximity to the radioactive grain, where the organic matter is coalified to semianthracite. A similar situation is observed near microfissures filled with radioactive minerals. Moreover, the temperature in both cases is the same. It is conceivable that precisely ionizing radiation is responsible for the notable coalification.

The influence of ionizing radiation on transformations of structural components of raw oil has been investigated in several experimental works [2]. Many works were devoted to the study of the structure of uranium-bearing bitumens [1–5] and the role of ionizing radiation in the synthesis of albuminous amino acids in solid bitumens [6]. The main purpose of these works was to study the influence of radiation on individual organic compounds or their classes. However, the mechanism of structural transformations in solid hydrocarbons (bitumens), which were subjected to the impact of high radiation doses, still remains unknown.

It is undoubted that the main role in structural transformations of solid bitumens belongs to temperature. At the same time, natural bitumens associate frequently with uranium-bearing minerals (for example, with thucholite). The content of radioactive elements (for example, U) in natural bitumens can be as high as 0.1%. Consequently, the decay of radioactive elements can contribute much to structural transformations of natural bitumens, as in case of coals [6].

We have studied changes in the molecular structure of solid hydrocarbons (bitumens) constituting the carbonization series (asphaltite–kerite–anthraxolite) under the influence of radiation (10 and 100 Mrad) by infrared spectroscopy (IRS). The radiation experiment was performed in the Arzamas-16 Federal Nuclear Center in line with conditions described in [6]. The IRS allows us to obtain reliable information on the molecular structure of solid hydrocarbons. Using characteristic or group frequencies of absorption, one can identify their different functional groups. The optical density of bands (A) in the IR spectra was determined by the method of reference lines based on peak heights. The contents of aliphatic, aromatic, condensed, and heterofunctional groups were estimated based on the sum of optical densities (ΣA) typical of the groups under consideration.

Gamma radiation of up to 10 Mrad on slightly metamorphosed solid bitumens of the *asphaltite* category substantially changed their molecular structures. In addition to the predominance of aliphatic components, the content of condensed structures is also increased in the molecular structures (Fig. 1a). As is known, the break of the C–H bond with the formation of phenyl radicals ($C_6H_5^*$) is the main possible trend in the breakdown of the excited aromatic molecule. The newly formed hydrogen atoms are rapidly captured by surrounding molecules to yield cyclohexadiene radicals ($C_6H_7^*$). Phenyl radicals can similarly react to form phenylcyclohexadiene radicals ($C_6H_4 - C_6H_7^*$). Subsequent reactions of recombination and disproportionation of radicals produce isomeric cyclohexadienes and polymeric condensed products. In addition, the radiolysis of aromatic hydrocarbons can yield polycyclic systems during bimolecular reactions of excited aromatic molecules.

The increase in the share of aliphatic groups (as compared with natural samples) is probably explained by the fact that alkyl radicals, which occur in the structure and/or form by radiation processes, interact to form aliphatic products with both higher and lower

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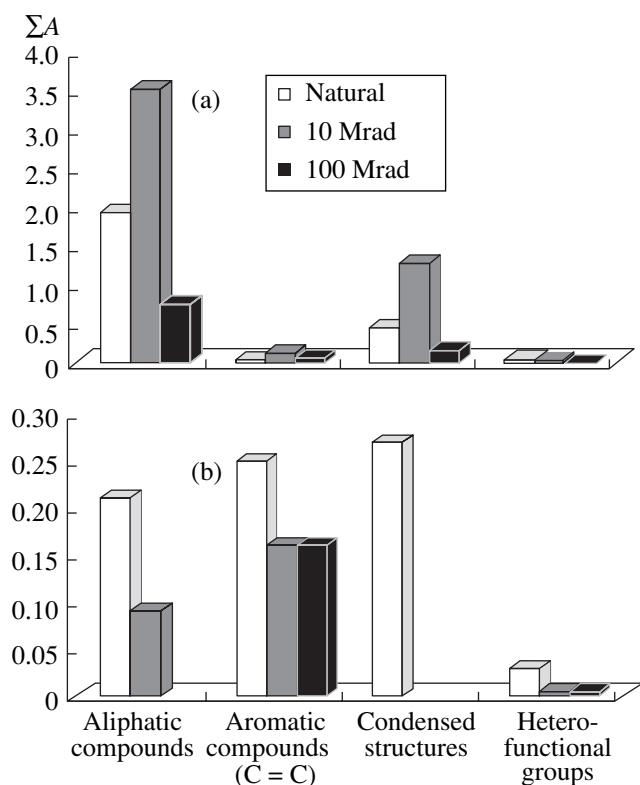


Fig. 1. Distribution of different functional groups in (a) asphaltite and (b) kerite structures.

molecular masses. This process is accompanied by the significant loss of heterofunctional groups, because they are usually less resistant to radiation than hydrocarbons. The loss of the functional group is one of the main processes that accompany their radiation.

An increase in radiation dose up to 100 Mrad results in further notable changes of the asphaltite molecular structure, which are reflected by the substantial loss of some aliphatic, aromatic, condensed, and heterofunctional groups. According to these spectral characteristics, the substance becomes similar to natural lower anthraxolites.

The IR spectra of kerites subjected to radiation of up to 10 and 100 Mrad appeared to be generally identical to each other in terms of the set and intensity of absorption bands. However, in addition to areas with the aromatic structure, some segments with the aliphatic structure (CH₂ and CH₃ groups) are also present in kerite subjected to radiation of up to 10 Mrad (Fig. 1b). These groups probably occur inside benzene rings or replace marginal hydrocarbon cycles.

The high radiation dose (up to 100 Mrad) resulted however in the complete loss of aliphatic groups. Like the radiated asphaltite samples, C=S functional groups remain in the structure of radiated kerites. This can be explained by the fact that sulfur takes an active part in polymerization and polycondensation processes. Consequently, this element may enter the structure of cyclic

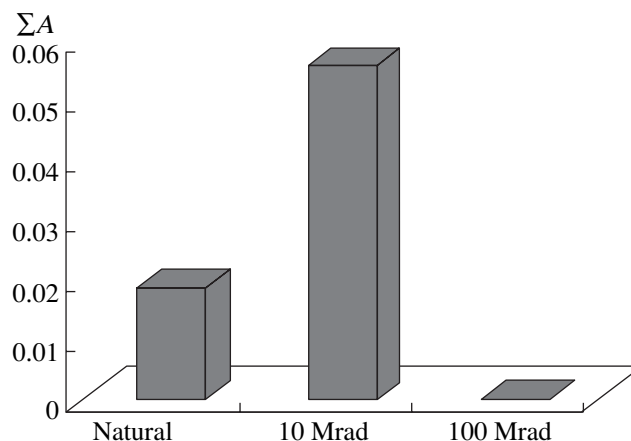


Fig. 2. Distribution of aromatic groups in the anthraxolite structure depending on the radiation dose.

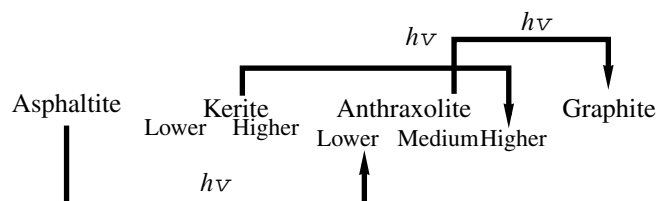


Fig. 3. Schematic transformation of solid bitumens in response to the radiation impact.

and aromatic compounds as a “stitcher.” In addition, oxygen-bearing groups of the C–O type are also present, although in insignificant quantities. It can be assumed that radioactive decay breaks down C–C bonds and produces C–O structures due to the linkage with oxygen atoms or the detachment of the hydrogen atom nearest to the functional group.

It should be noted that natural kerites represent a complex combination of planar polycyclic and linear (aliphatic) areas with different degrees of their structure ordering [3]; i.e., they contain substantially more aromatic fragments than asphaltites. The content of C=C oscillation groups in the benzene ring is probably retained owing to the high radiation resistance of benzene in the IR spectra of kerites subjected to radiation. In general, the structure of radiated kerites demonstrates features typical of natural high anthraxolites.

Absorption bands disappear as a result of the increase in the carbon content in the bitumen structure and the consequent increase in the share of aromatic rings. Therefore, the IR spectra of anthraxolites after the radiation impact become similar to those of graphites, although the IR spectra of anthraxolites subjected to radiation of up to 10 Mrad still demonstrate weak absorption bands characteristic of the benzene ring (Fig. 2).

Thus, the results show that, in addition to temperature, radiation can also affect the process of coalifica-

tion. Using carbonization of the asphaltite–kerite–anthraxolite series as an example, we have established that traces of the influence of high-energy radiation on a substance are reflected in the modification of its structure and the appearance of features similar to those of graphite (Fig. 3).

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REFERENCES

1. A. I. Zubov, *Geol. Rudn. Mestorozhd.*, No. 5, 6 (1960).
2. N. M. Likhterova, V. V. Lunin, V. N. Torkhovskii, et al., *Khim. Tekhnol. Topliv Masel*, No. 4, 32 (2004).
3. V. G. Melkov and A. M. Sergeeva, *Role of Solid Carbonaceous Substances in the Formation of Endogenic Uranium Mineralization* (Nedra, Moscow, 1990) [in Russian].
4. V. F. Pen'kov, *Uranium and Hydrocarbons* (Nedra, Moscow, 1989) [in Russian].
5. V. F. Pen'kov, *Genetic Mineralogy of Carbonaceous Substances* (Nedra, Moscow, 1996) [in Russian].
6. N. P. Yushkin, *Vestn. Inst. Geol.*, No. 9, 2 (1999).